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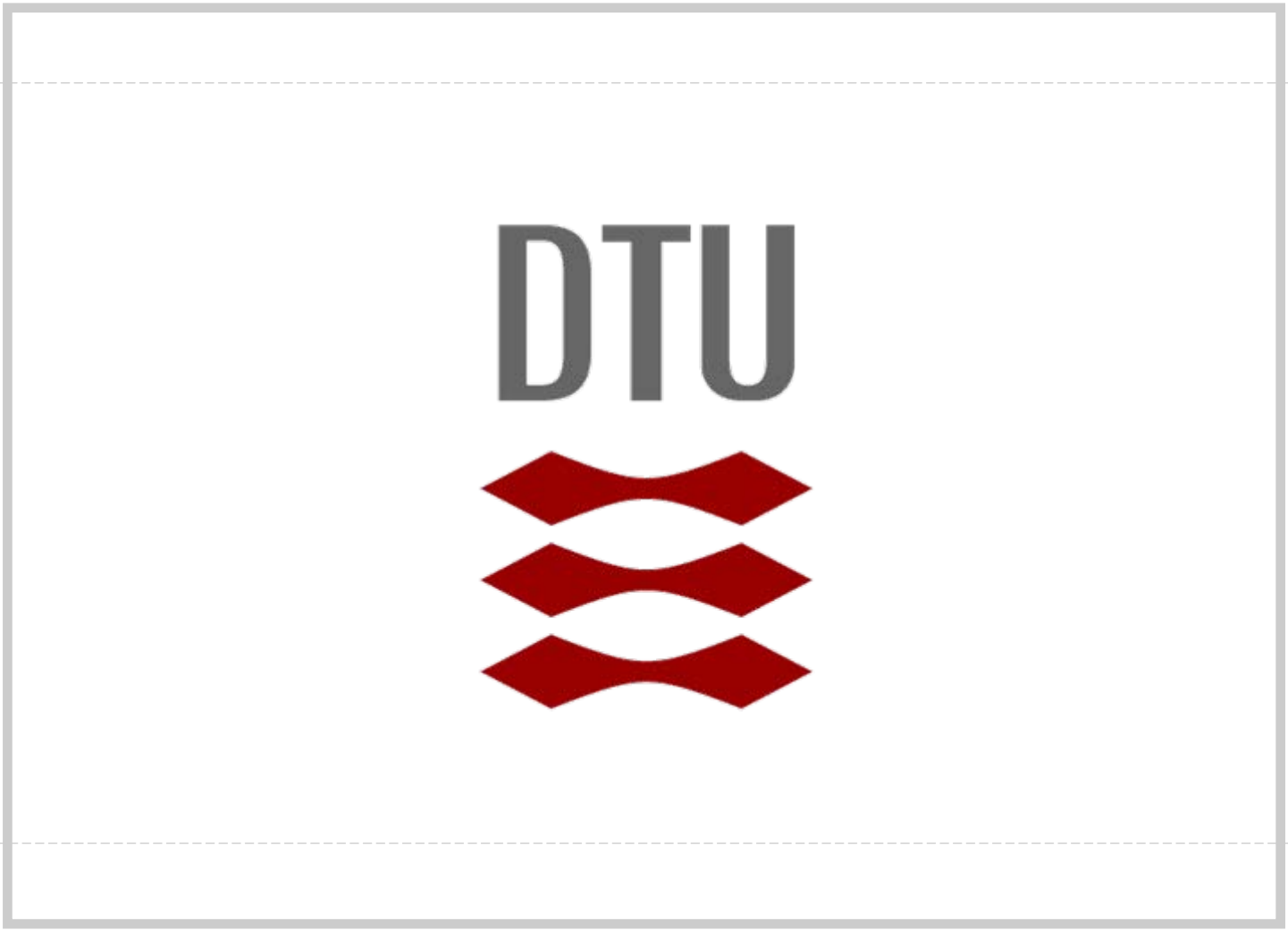
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# A new role of Proficiency Testing in Nuclear Analytical Work

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# *In the beginning was the word.....*

*(Joh.1:1)*

## *and the word was **uncertainty***

- *but some people did not like it, and*
- *those who did could not use it, because we were not sure of its meaning*

# International Vocabulary of Basic and General Terms in Metrology

VIM
2nd Edition
1993

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# 1. axiom

- A result

*without statement of uncertainty*

**is useless**

*because no valid conclusions* can be *reached*

# Guide to the Expression of Uncertainty in Measurement

GUM
1st Edition
1995

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# Evaluation of Sampling Uncertainty

- **Type A**

statistical analysis of actual observations

- **Type B**

any other method

# 2. axiom

- A result

*with an incorrect statement of uncertainty*

**is dangerous**

*because erroneous conclusions may be reached*

# Accreditation after ISO 17025*

- Correct measurement results:
  - no significant bias
  - reliable uncertainty

*or ISO 15189

# Proficiency Testing

ISO 13528:

**Statistical methods for use in proficiency testing by interlaboratory comparisons**

**Laboratory Bias**



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# International Vocabulary of Basic and General Terms in Metrology

VIM
3rd Edition
2007

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# Measurand

# VIM 3

***quantity** intended to be measured*

- *this definition differs from VIM 2*
- *must include exact specifications*

# Definition of the Measurand I

- The *determinand, i.e.*

  the chemical species to be determined

- The *specified amount of material*

  to which the measurement should apply

# Quantity value

# VIM 3

***Magnitude** of a quantity*

*expressed as a product of*
*a number and a unit*

# Measurement Result VIM 3

Information on the measurand consisting of

- *a single* ***quantity value , y*** *and*
- *a* ***measurement uncertainty, u***



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# Definition of the Measurand II

- A result without corresponding definition of the measurand is worthless
- An uncertainty without corresponding specification of the measurand is misleading

# Initial proficiency requirements I

*1) Definition of the measurand, incl. identification of the determinand and specification of the system*

*2) Choice of analytical measurement method and detailing a procedure yielding traceable results*

*3) Development of an uncertainty budget, including correct application of counting statistics*

*4) Partial verification of uncertainty budget by replicate analyses*

# Final proficiency requirements II

5) *Choice of sampling strategy and number of samples to be analyzed*

6) *Reporting results of analyses corrected for bias and with specified coverage interval.*

7) *Final verification of analytical results and their uncertainties by proficiency testing*

8) *Calculation of the $E_n$ number*

# Our null hypothesis is now that

*All reported measurement results for proficiency testing comply with these stipulations, so that*

*traceability is consistent with the definition of the measurand*

*all known biases have been corrected for*

*uncertainties are based on a verified uncertainty budget with a large number of effective degrees of freedom*

# Bayesian estimate of mean

$$\hat{\mu} = \frac{\sum_i \omega_i \cdot y_i}{\sum_i \omega_i}$$

where $\omega_i = u_i^{-2}$ and $u_\mu = \sqrt{\frac{1}{\sum_i \omega_i}}$

# Test statistic

$$T = \sum_i \frac{(y_i - \hat{\mu})^2}{u_i^2}$$

*Chi-square distribution*
*with n-1 degrees of freedom*

# $E_n$ numbers

$$E_n^{(i)} = \frac{y_i - \hat{\mu}}{\sqrt{U_i^2 + U_\mu^2}}$$

$$U \sim 2u$$

# “bottom up” strategy

*a) expanded uncertainties, U, are converted to standard uncertainties, u = U/k*

*b) measurement results are ordered according to decreasing u*

*c) results are added in this order one at a time, and a value of T is calculated*

*d) if $T \leq \chi 2_{\alpha,m-1}$ the next measurement result is added*

# “bottom up” strategy

*e)* *if $T > \chi 2_{\alpha,m-1}$ the result with the largest contribution to T is removed*

*f)* *after reaching the end of the list go back to c) and add results previously removed*

*g)* *repeat c) to f) until there is no change in the selected group of measurement results*

*h)* *calculate the reference value $\mu$ and its uncertainty $u_{\mu}$*

$\hat{\mu}$

# “top down” strategy

*a) apply robust algorithms A and S [3] to the $y_i$ data for estimating $\mu$, respectively their uncertainties $U_i$ for estimating $U_\mu$*

*b) calculate $E_n$ numbers and disregard all results with $|E_n|>1$,*

*c) calculate the weighted mean of the remaining results, using $1/U_i^2$ as weights*

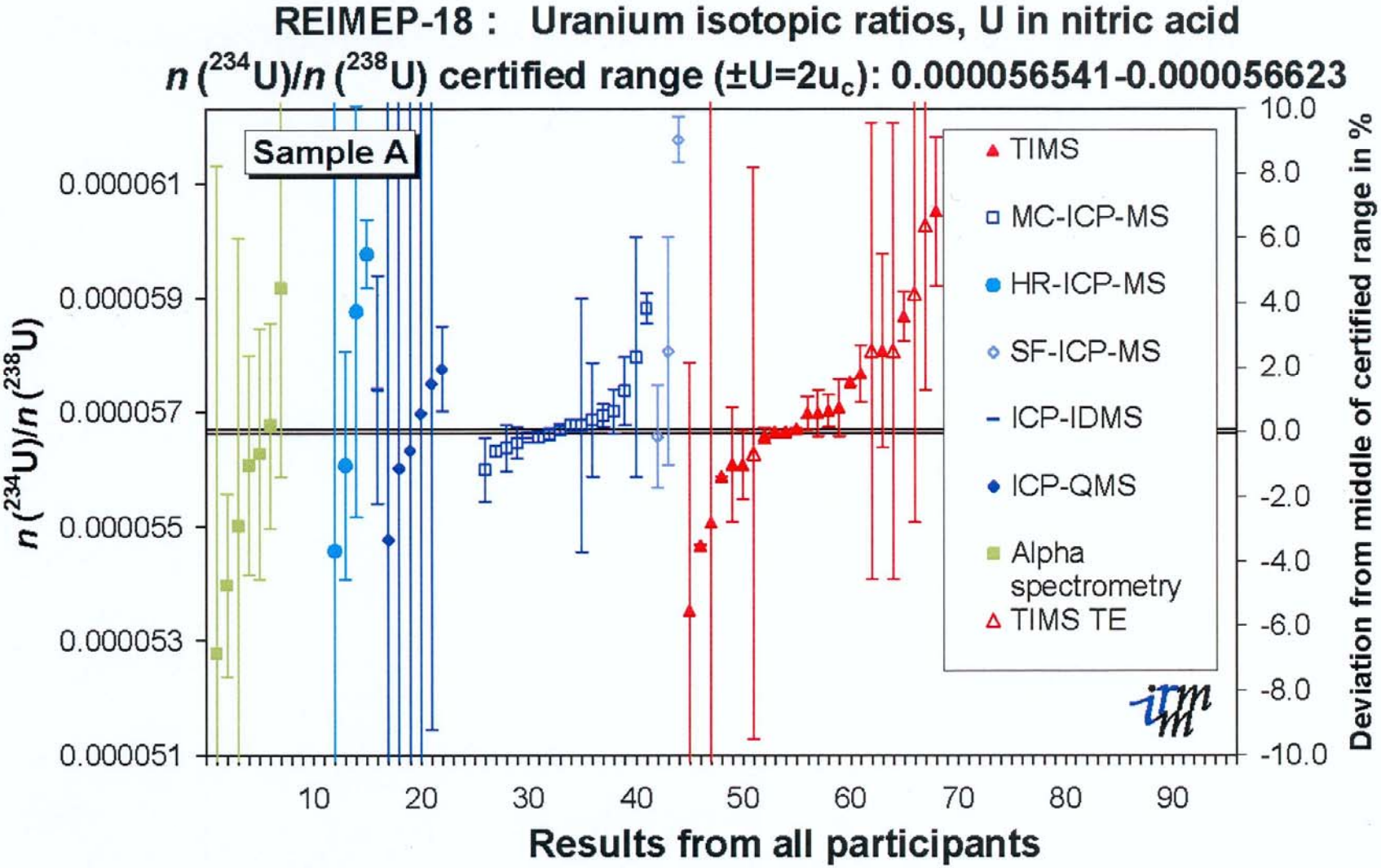
# “top down” strategy

*d) calculate its corresponding uncertainty from*

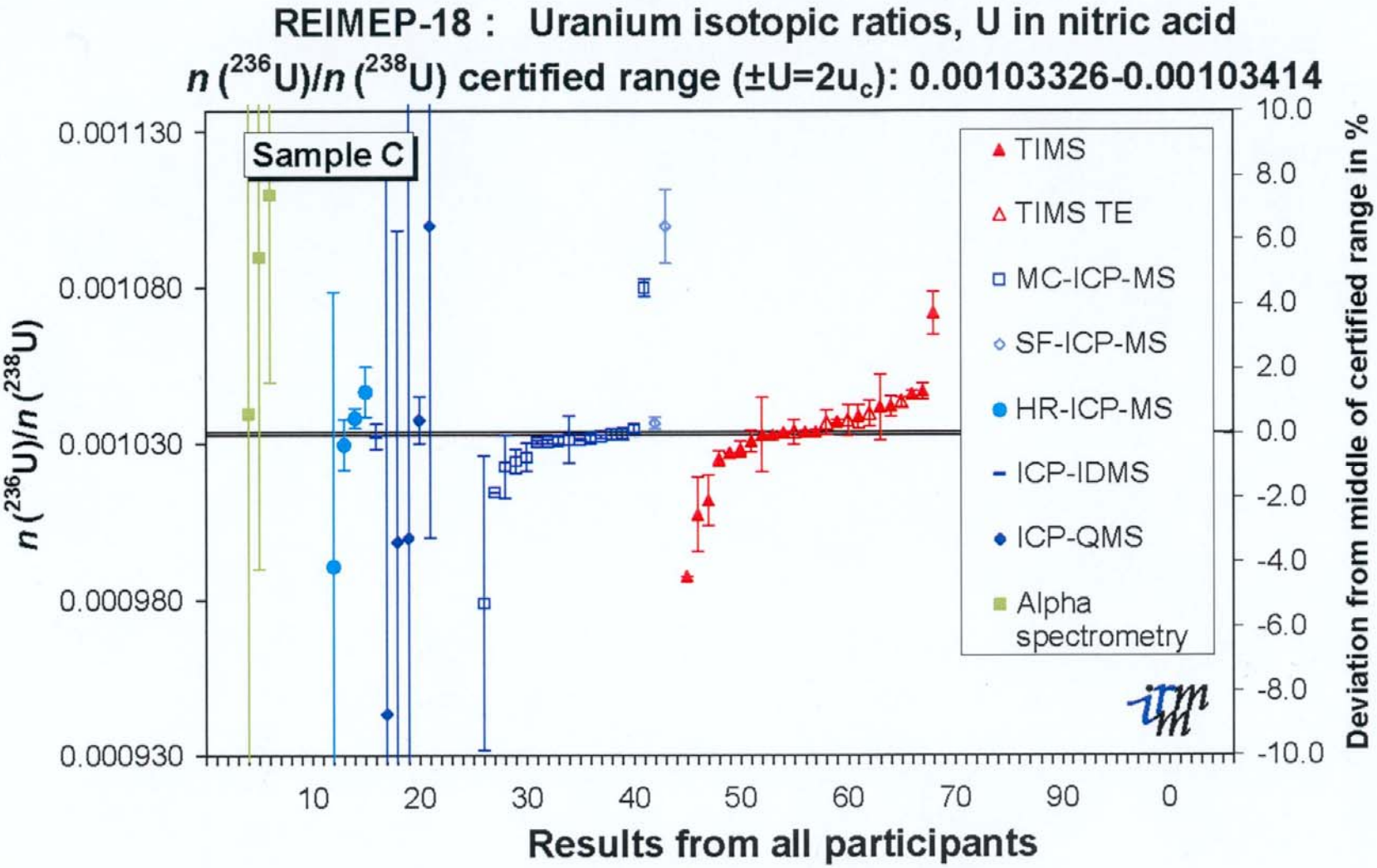
$$U_{\mu}^{-2} = \sum U_{i}^{-2}$$

*e) repeat b) to d) until there is no change in the selected group of measurement results*

*f) use their weighted mean as reference value and $U_{\mu}$ as its expanded uncertainty.*




Results for the $n(^{234}U)/n(^{238}U)$ ratio for REIMEP 18 A




Results for the $n(^{236}U)/n(^{238}U)$ ratio for REIMEP 18 C

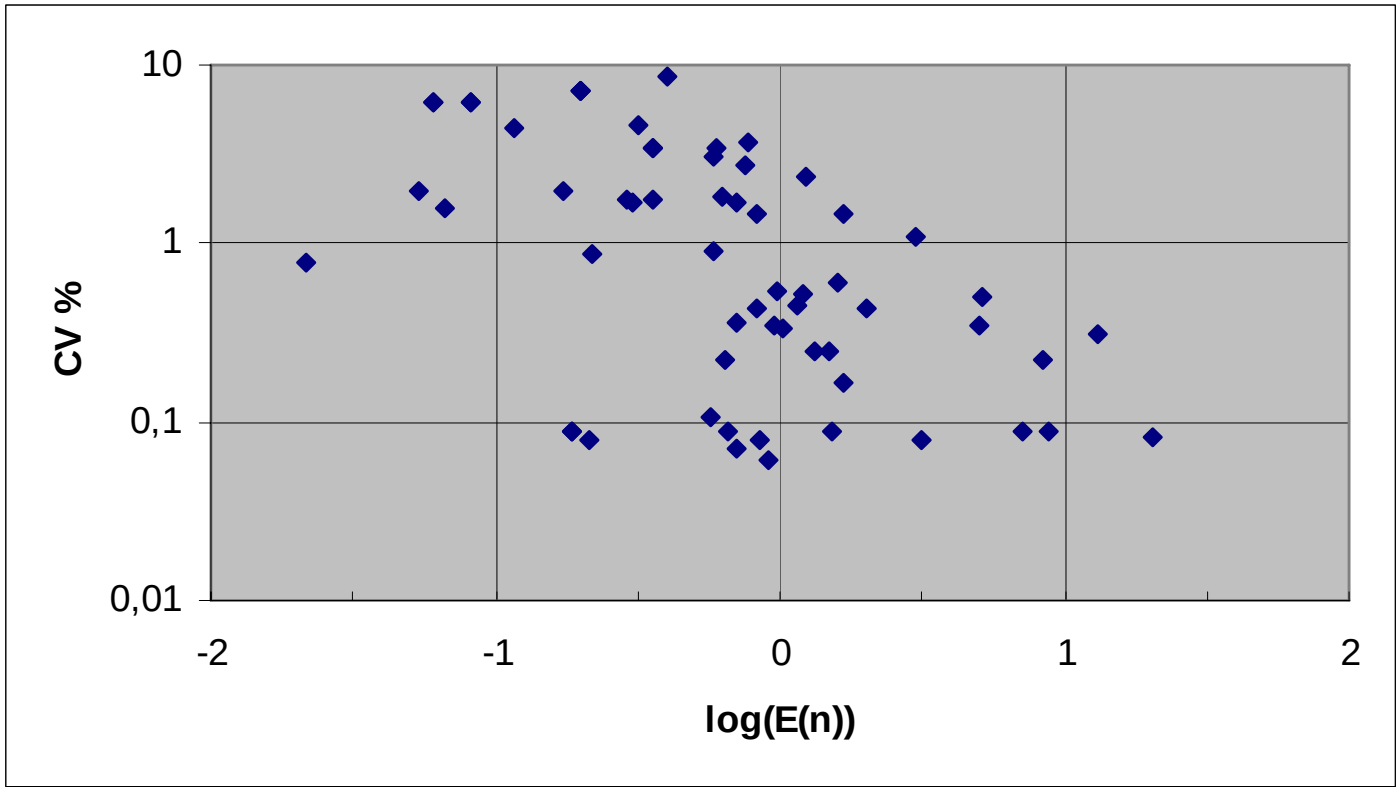
# Reference values for Uranium isotopic ratios

| Strategy | $^{234}U/^{238}U$ value ±Uncertainty (k=2) | Results accepted | $^{236}U/^{238}U$ value ±Uncertainty (k=2) | Results accepted |
|---|---|---|---|---|
| Bottom up | 0.000056581±31 | 42 | 0.00103368±51 | 27 |
| Top down | 0.000056609±37 | 39 | 0.00103390±54 | 25 |
| Combined | 0.000056581±31 | 42 | 0.00103368±51 | 27 |

# Correct measurement results

- Participants
- Methods

# $^{234}U/^{238}U$ proficiency data



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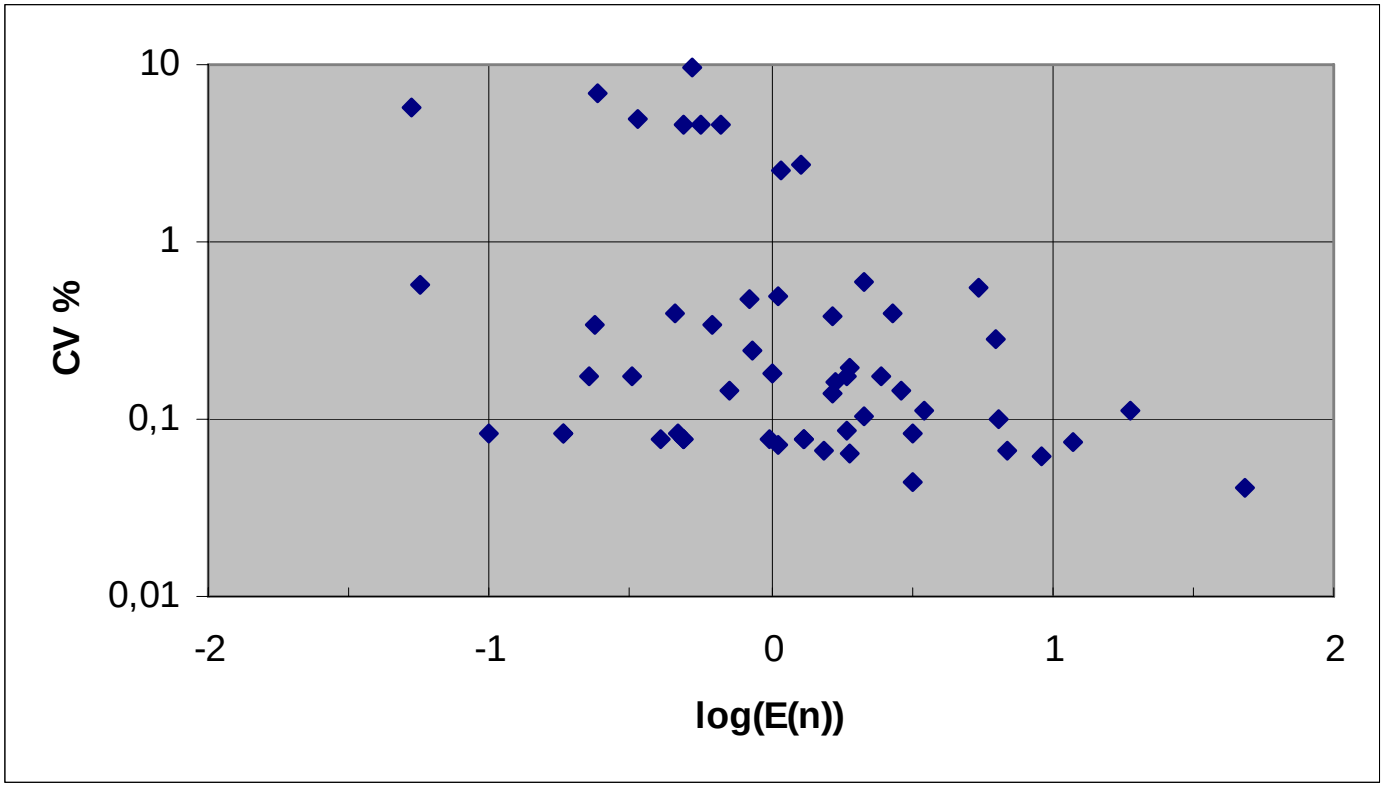
# $^{236}U/^{238}U$ proficiency data



# Median of $E_n$ numbers for analytical methods

| Technique | Sample A Median | Number results | Sample C Median | Number results |
|---|---|---|---|---|
| Alpha | -0,31 | 7 | 0,56 | 3 |
| HR-ICP | 0,20 | 4 | 0,59 | 4 |
| ICP-IDMS | 0,36 | 1 | -0,32 | 1 |
| ICP-QMS | -0,01 | 6 | -0,24 | 5 |
| MC-ICP | 0,14 | 16 | -1,06 | 16 |
| SF-ICP | 0,71 | 3 | 3,70 | 2 |
| TE | 0,35 | 5 | 1,45 | 4 |
| TIMS | 0,66 | 19 | 0,34 | 20 |

# VIM 3 is a major challenge in

- Our way of interpreting analytical data

  Co-operate with the client to define fitness for purpose

- Our way of treating proficiency data

  Accreditation authorities beware of the uncertainty of assigned values

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# Question from the audience:

- Would the proposed method lead to substantially different $E_n$ numbers?

- Not for the particular example used here, but for the example used in ISO 13528 the drastic reduction of the uncertainty of the reference value greatly increases the detection capability for too optimistic reported uncertainties.

# Comparison with certified values

| Value | $^{234}U/^{238}U$ value ±Uncertainty (k=2) | Results accepted | $^{236}U/^{238}U$ value ±Uncertainty (k=2) | Results accepted |
|---|---|---|---|---|
| Reference | 0.000056581±31 | 42 | 0.00103368±51 | 27 |
| | | | | |
| Certified | 0.000056582±41 | Sample A | 0.00103370±44 | Sample C |

# Reference values* for Pb in IMEP-9

| Method | Reference value ± Uncertainty | Number of accepted results | Comment |
|---|---|---|---|
| Synthesis of Precision | 617.7 ± 2.7 | 60 | Recommended |
| $E_n$ numbers | 614.1 ± 3.2 | 59 | Alternative |
| Robust average | 605 ± 26 | 181 | ISO 13528 (2005) |
| ICP-MS | 623 ± 13 | 6 | Certified value |

***in units of $10^{-10}$ mol/L**